

CHARACTERIZATION OF NITROGEN COMPOUNDS IN TAR
PRODUCED FROM UNDERGROUND COAL GASIFICATION

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INTRODUCTION

In the fall of 1972, the Laramie Energy Research Center of the Bureau of Mines (now the Energy Research and Development Administration) initiated an in situ coal gasification experiment in Hanna, Wyoming. The objective was to ascertain if a low-Btu gas which would be competitive with other energy sources could be produced using present technology. If such a process were feasible it could provide an alternative to the hazards, costly transportation, and environmental objections of current coal mining technology.

The idea of underground coal gasification is over a hundred years old and has been tried in several different countries, with the largest experiments in the USSR, Great Britain and the U. S. These experiments showed that gasification was possible and a combustible fuel could be produced, yet the British and U. S. trials were determined to be economically impractical at the time they were conducted. Although information is sketchy, the USSR is presently generating electricity from low-Btu gas generated via in situ gasification. It is claimed that this power is generated at costs competitive with coal fired power plants.

DESCRIPTION OF THE UNDERGROUND GASIFICATION EXPERIMENT

The Hanna, Wyoming, experiment (1-3) was conducted in a subbituminous coal seam thirty feet thick at a depth of four hundred feet. A pattern of sixteen wells was drilled into the seam to take advantage of the natural fractures and permeability of the coal. In March 1973 the coal was ignited and air was supplied as the gasification agent. After initial start-up a steady-state system was obtained which lasted from September 1973 through February 1974. During this six-month period, gas analyses were taken along with other operating data. A low-Btu gas averaging approximately 130 Btu/scf was produced and the production was controlled to some degree by varying pressure and flow rates of the air injected and the gases produced.

In conjunction with low-Btu gas production, a liquid product was condensed from the gas stream. The major part was water but approximately 10% was an organic layer or coal tar. This coal tar has been estimated to contain 5% of the total energy produced from the in situ system. This coal tar raised three questions. What was its value as a petroleum substitute, either as a fuel or as a petrochemical feedstock? What information could be derived from this coal tar concerning reaction conditions occurring in the coal seam? Did the coal tar contain compounds which may lead to environmental damage? Characterization of these coal tars was therefore undertaken in an attempt to answer these questions.

During the period of gas production coal tar samples were collected from the produced gas stream. The liquid condensate, composed of coal tars and water, was separated in an air cooled condenser and a portion was drawn off as a sample. Two of these samples which represented distinctly different operating conditions during the life of the in situ coal gasification experiment were chosen for characterization.

The dry gas production rate over an eight-month period is shown in Figure 1 with the collection dates for samples 1 and 2 shown. As can be seen, Sample 1 was taken during a period of low gas production, which is associated with carbonization rather than gasification. Sample 2 was taken during a period of high gas production when the contribution of gasification was greater. A further indication of the relative contributions of carbonization and gasification can be seen from the gas analyses shown in Table 1 for the dates of coal tar sample collection. The carbonization of coal produces a large amount of methane compared to the amount of carbon monoxide. Upon reaching the conditions required for gasification, the carbon monoxide produced will increase due to the reactions shown by Equations 1 and 2.



TABLE 1. - Gas Analyses on Collection Dates

	Sample 1 August 4, 1973	Sample 2 December 10, 1973
Hydrogen	9.5 ^a	16.14
Argon	1.17	1.01
Nitrogen	55.62	53.84
Methane	9.62	3.74
Carbon Monoxide	0.80	6.94
Ethane	0.81	0.28
Carbon Dioxide	21.90	17.91
Propane	0.16	0.08
Propene	0.12	0
n-Butane	0.01	0
iso-Butane	0.05	0
Hydrogen Sulfide	0.23	0.05
Heating Value	154 Btu/scf	119 Btu/scf

^aValues are expressed in mole %

The high ratio of methane to carbon monoxide in the product gas on the collection date for Sample 1 indicates that carbonization is the primary reaction mode. Conversely, the low ratio of methane to carbon monoxide on the collection date for Sample 2 indicates that gasification was occurring to a greater degree.

Experimental

Nonaqueous titration of nitrogen was performed in acetic anhydride and benzene with HClO_4 as described by Buell (4). GLC analyses of tar bases were done on a 15' x .18" 15% TRITON X-305 on a Gaschrom P column. With a helium carrier gas, a flow rate of 46 ml/min STP, isothermally at 100°C for 16 min, then a 2°C/min

increase to 220°C, a useable separation of components resulted. NMR spectra were recorded on a Varian HA-100 instrument with the use of a Varian C1024 (CAT) console for one specific sample. UV spectra were recorded on a Beckman DB-G spectrometer with cyclohexane as solvent. Mass spectra were obtained on an AEI MS-12 instrument. Simulated distillations were performed with use of gas chromatography with residue defined as any material that does not boil below 1000°F. Fractionalization into tar acid, tar base and neutral fractions was accomplished by mineral acid and sodium hydroxide extraction and then regeneration through pH adjustment.

Coulometric nitrogen determination was performed on a Dohrmann instrument by reductive pyrolysis and subsequent ammonia titration in a microcoulometer. Coulometric sulfur determination was obtained using a Dohrmann instrument by oxidative pyrolysis to sulfur dioxide and titration of the sulfur dioxide in a microcoulometer.

COAL TAR CHARACTERIZATION

Each sample was subjected to analyses by simulated distillation, nonaqueous titration, and elemental analysis, plus determination of some physical properties. Upon separation of both samples into tar base, tar acid and neutral fractions, each fraction was then subjected to nonaqueous titration and coulometric determination of nitrogen and sulfur. The tar base fractions from both samples were separated by GLC where compound types have been assigned to separated components with specific structures identified in some cases.

Simulated Distillations

Simulated distillations showed Sample 1 to have a boiling range of 100-600°F with no residue. Sample 2 had a boiling range of 100-950°F with no residue. The percentage of the coal tar within a specified boiling range is shown in Table 2. As Table 2 shows, over 50% of sample 2 has a boiling distribution between 500°F and 700°F, while sample 1 has almost 50% of the boiling range distribution between 400°F and 500°F. This shows that sample 1 was a lighter coal tar than sample 2 and that the average molecular weight of sample 1 was less than sample 2.

TABLE 2. - Boiling Range Distribution

Sample	100 - 400°F	400 - 500°F	500 - 600°F	600 - 700°F	700 - 800°F	800 - 900°F	900 - 1000°F	Residue
1	30.0%	46.7%	22.0%	1.3%	0%	0%	0%	0%
2	6.2	16.9	25.6	28.2	16.0	5.3	1.8	0
Carbonized	0	11.3	16.3	13.1	15.2	12.4	7.5	24.2

For comparison, the boiling range distribution for the coal tar produced by laboratory carbonization of a Hanna coal sample at 500°C is presented. In comparing the distribution of material depicted in Table 2 the relative amount of residue becomes evident. Samples 1 and 2 show no residue while nearly a fourth of the carbonized sample is residue or material boiling above 1000°F. This demonstrates a unique fact concerning these coal tars. While the underground gasification may be similar to aboveground gasification, the coal tars produced in underground gasification are carried to the surface as a steam distillate. Since very little heavy tar will reach the surface, under these conditions, very little if any residue is expected, and the coal tar will not be entirely representative of the total tar generated in the combustion zone.

Nonaqueous Titrations

Nonaqueous titrations of samples 1 and 2 are shown in Table 3.

TABLE 3. - Nonaqueous Titrations of Samples 1 and 2

Sample 1	0.665% WB ^a	0.129% VWB ^a
Sample 2	0.524% WB	0.186% VWB

^aWB and VWB refer to weak and very weak base

Strong, weak, and very weak bases are defined by their half neutralization potentials (HNP), with strong bases having an HNP less than 150 mV, weak bases between 150 and 350 mV, and very weak base greater than 350 mV. Examples of weak bases would be pyridines or quinolines while amides would be titrated as very weak bases. Primary and secondary anilines titrate as very weak bases since they will acetylate and then titrate as amides. It should be understood that not all nitrogen compounds will titrate. Conversely not only nitrogen containing compounds will titrate, as an example, some sulfoxides titrate as very weak bases.

Physical Properties

Some of the physical properties of samples 1 and 2 are shown in Table 4. As expected from the conclusions of the simulated distillations, sample 2 is a heavier sample. The higher specific gravity, viscosity and heat of combustion all indicate that Sample 2 does indeed represent a higher average molecular weight coal tar.

TABLE 4. - Physical Properties

	Sample 1	Sample 2
Specific gravity at 60°F	0.962	0.977
Viscosity at 100°F	3.55 centistokes	13.16 centistokes
Heat of Combustion	16,073 Btu/lb	17,256 Btu/lb

Elemental Analyses

The elemental analyses of samples 1 and 2 indicate a marked difference in oxygen content as shown in Table 5.

TABLE 5. - Elemental Analyses

	Sample 1	Sample 2
Carbon	77.80	86.33
Hydrogen	10.22	10.43
Nitrogen	0.74	0.79
Sulfur	0.23	0.18
Oxygen	11.04 ^a	2.27 ^a

^aOxygen percentage is determined by difference

This change in oxygen content is attributed to the relative amounts of tar acids in each sample. This is shown in Table 6, where the composition of samples 1 and 2 vary noticeably with respect to the relative amounts of tar acids. Preliminary mass spectral analysis of the tar acid fraction from Sample 1 showed the majority of the fraction to be substituted phenols which would help explain the higher oxygen content in sample 1 compared to sample 2.

TABLE 6. - Composition of Coal Tar, by Weight Percent

	Sample 1 ^a	Sample 2 ^b
Tar Base	4.0	8.7
Tar Acid	42.1	14.5
Neutral	53.9	76.8

^a90.9% recovery of sample 1

^b96.4% recovery of sample 2

The difference in tar acid content between the two samples is proposed to be due to some basic change in the conditions producing the two samples. At the time Sample 1 was produced, the air injection rate into the combustion zone was considerably less than at the time Sample 2 was formed. Higher air injection rates are associated with higher coal utilization, higher gas production rate, and higher exit temperature of the produced gas. This would suggest that the coal tars collected in Sample 2 either were being formed at higher temperatures or were passing through a higher temperature flame front (combustion zone). Fieldner and Davis (5) have reported a change in composition of coal tar with increasing carbonization temperature. They stated that increasing temperature causes a decrease in tar acid content which agrees with the comparison of Samples 1 and 2 (Table 6). With the increase in boiling range and other parameters measured during the experiment, this evidence indicates that Sample 2 was indeed produced at a higher temperature than Sample 1.

Total Nitrogen, Total Sulfur and Nonaqueous Titration
of Base, Acid and Neutral Fractions

The results of coulometric determination of nitrogen and sulfur plus the nonaqueous titrations of the tar base, tar acid and neutral fractions of samples 1 and 2 are shown in Table 7.

TABLE 7. - Total Nitrogen, Total Sulfur, and Titratable Nitrogen for Acid, Base and Neutral Fractions

	Total Sulfur	Total Nitrogen	Titrateable Nitrogen ^a
Sample 1			
Tar Base	0.00%	9.64%	8.10% WB, 1.36% VWB
Tar Acid	0.33	0.35	0.264% WB, 0.081% VWB
Neutral	0.02	0.08	0.035% VWB
Sample 2			
Tar Base	0.23	4.82	4.45% WB, 0.36% VWB
Tar Acid	0.14	0.09	0.058% VWB
Neutral	0.20	0.37	0.037% WB, 0.145% VWB

^aWB and VWB refer to weak and very weak base

As can be seen from Table 7, the distribution of sulfur in the separate fractions seems to be random and therefore no conclusions have been drawn as to their compound types or explain their distribution. An interesting point about the nitrogen values is the fact that while sample 2 contains approximately twice the weight percent tar base that sample 1 contains, the total nitrogen of sample 2's tar base fraction is about half that of sample 1's tar base fraction. This would suggest that the tar bases in sample 2 have a higher average molecular weight than those of sample 1.

The nonaqueous titrations of the two different tar base fractions indicate the possibility of pyridines and quinolines as weak bases with the added possibility of anilines titrated as very weak base.

Identification of Selected Components in the Tar Base Fraction

Twelve different components were fractionated by GLC from Sample 1 and spectral data were obtained on each. These twelve peaks constituted 69% of the base fraction of Sample 1. Compound types have been assigned to all separated components and specific structures in some cases. Assignments were accomplished with the combined aid of NMR, MS, UV and GLC data. The results are tabulated in Table 8.

TABLE 8. - Tabulated Spectra on Separated Components From
Tar Base Fraction of Sample 1

Component	t_R^a	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
1	8.9	1.18%	Triplet- δ 7.10; Triplet- δ 7.50; Doublet- δ 8.45	λ_{max} at 262 nm	100% m/e 79	pyridine
2	11.0	6.40	Singlet- δ 2.41; Quartet- δ 6.95; Triplet- δ 7.36; Doublet- δ 8.33	λ_{max} at 257 nm	100% m/e 93	2-picoline
3	13.1	6.20	Singlet- δ 2.37; Doublet- δ 6.74; Triplet- δ 7.24	λ_{max} at 260 nm	100% m/e 107	2,6-lutidine
4	14.9	9.61	Triplet- δ 1.24; Singlet- δ 2.24; Quartet- δ 2.72; Multiplet- δ 6.98; Multiplet- δ 7.35; Singlet- δ 8.30	λ_{max} at 255 nm	90% m/e 93 10% m/e 107	3-picoline, 4-picoline and 2-ethyl pyridine
5	17.3	12.90	Triplet- δ 1.21; Singlet- δ 2.17; Singlet- δ 2.36; Quartet- δ 2.65; Multiplet- δ 6.77; Multiplet- δ 7.22; Doublet- δ 8.17	λ_{max} at 258 nm	90% m/e 107 8% m/e 121	2,4-lutidine, 2,5-lutidine plus some methyl ethyl pyridine
6	18.3	3.22	Singlet- δ 2.18; Singlet- δ 2.36; Multiplet- δ 6.81; Doublet- δ 7.19; Singlet- δ 8.15	λ_{max} at 263 nm	90% m/e 107	2,3-lutidine

TABLE 8. - Tabulated Spectra on Separated Components From Tar Base Fraction of Sample 1 (Continued)

Component	t _R ^a	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
7	19.2	7.11	Triplet- δ 1.21; Singlet- δ 2.14; Singlet- δ 2.32; Quartet- δ 2.59; Singlet- δ 6.58; Doublet- δ 7.34	λ_{\max} at 262 nm	15% m/e 107 79% m/e 121	trimethyl pyridine and an ethyl pyridine
8	31.1	5.98	Broad Singlet- δ 3.36; Quartet- δ 6.52, Triplet- δ 6.96	λ_{\max} at 283 nm λ_{\max} at 231 nm	93% m/e 93	aniline
9	34.7	4.88	Singlet- δ 2.15; Broad Singlet- δ 3.28; Multiplet- δ 6.32; Triplet- δ 6.84	λ_{\max} at 285 nm λ_{\max} at 235 nm	97% m/e 107	2-methylaniline
10	38.1	2.54	Triplet- δ 1.15; Singlet- δ 2.10; Quartet- δ 2.45; Broad Singlet- δ 3.32; Multiplet- δ 6.25; Triplet- δ 6.86	λ_{\max} at 286 nm λ_{\max} at 235 nm	92% m/e 121	a dimethyl aniline and an ethylaniline
11	39.1	4.08	Doublet- δ 1.15; Singlet- δ 2.05; Multiplet- δ 6.10 to δ 8.10; Singlet- δ 8.80	λ_{\max} at 313 nm λ_{\max} at 270 nm	63% m/e 129; 16% m/e 121; 9% m/e 135; 8% m/e 94	quinoline, a dimethyl aniline and a trimethyl aniline
12	40.5	5.02	Triplet- δ 1.12; Quartet- δ 2.40; Singlet- δ 2.62; Doublet- δ 2.75; Multiplet- δ 7.04 to δ 8.00; Singlet- δ 8.78	λ_{\max} at 315 nm; λ_{\max} at 265 nm	45% m/e 143; 22% m/e 135; 17% m/e 129; 12% m/e 157	a methyl quinoline, a C ₃ aniline; quinoline, a dimethylquinoline

^aGLC retention times are relative to air

As can be seen from the data presented, all the components separated were not pure compounds, but a compound type can be determined from the spectrographic data. The resolution of the GLC tended to drop off as the heavier components were eluted. Due to the more complex nature of their spectra and the greater number of possible structures, specific structures have not been assigned to some of these heavier components.

46.6% of the base fraction was substituted pyridines, 13.4% anilines, and 9.1% quinolines. The majority of the remainder is probably substituted pyridines since

they are eluted after component #7 and before #8 which is aniline. Comparing this analysis with the work of Karr, et.al. (6), who found the majority of the tar base fraction of a low temperature coal tar to be quinolines, indicates that this coal tar was produced under conditions other than those producing low temperature coal tars.

The base fraction from Sample 2 was also subjected to identical GLC analysis as the base fraction from Sample 1. This sample also showed a wide distribution of components except that the majority of the fraction was much heavier than that from Sample 1. The GLC trace indicated six resolved peaks with retention times from 39.5 to 46.6 constituting approximately 45% of the base fraction. Comparing these retention times with those in Sample 1 suggests that these components are alkylated anilines or quinolines.

NMR spectra of five of these six peaks indicate these components to be substituted quinolines. As yet, no specific structures have been assigned to any of the peaks. This would agree with Karr's work and would suggest that the coal tars are formed under low temperature conditions. However, with other evidence already presented, such as boiling range, production rates, gas exit temperatures and tar acid content, it is believed that Sample 2 could not have been produced at lower temperatures than Sample 1.

CONCLUSIONS

In summary, the composition of the coal tar, particularly the basic fraction, is reasonably well known. A decision on its use as a petrochemical feedstock might be made from this information. However, the conditions under which the coal tar is produced are still unknown. Improved monitoring of the combustion zone, especially temperatures, will be included in future experimentation at Hanna. Data from this additional monitoring should allow more definite conclusions to be drawn. Possible herbicidal properties of components identified would require precautions against spillage to minimize environmental impacts. Monitoring underground migration of these organic fluids to determine what effect they may have on water supplies is being studied.

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NOTE: Any reference to specific brand names does not imply endorsement by the Bureau of Mines.

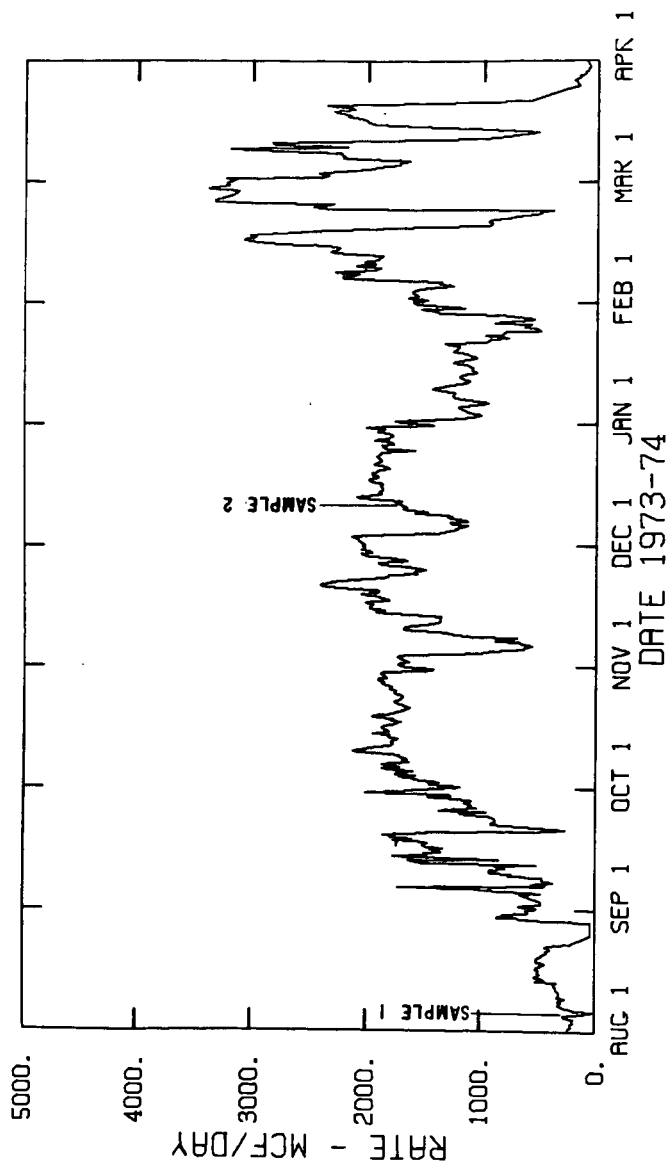


FIGURE 1. - DRY GAS PRODUCTION RATE, UNDERGROUND COAL GASIFICATION
EXPERIMENT, HANNA, WYOMING